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PAPER

Evolution of the charge carrier plasmon in the one-dimensional metal TTF-TCNQ as a function of temperature and momentum

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Abstract

We have investigated the charge carrier plasmon in the quasi one-dimensional metal TTF-TCNQ using electron energy-loss spectroscopy. Our data reveal a negative plasmon dispersion with a slope that is independent of temperature, which is in agreement to predictions from model calculations and previous room temperature data. A plasmon energy shift upon temperature is observed, and we discuss possible contributions to this shift. The spectral width of the plasmon is rather temperature independent, but increases clearly above a momentum value of about 0.3 $\mathring{A}^{-1}$.

1. Introduction

Charge transfer salts consisting of molecular species form a wide class of materials and exhibit a variety of interesting electronic and magnetic properties [1, 2]. The compound TTF-TCNQ (tetrathiafulvalene-tetracyanochinodimethane) is one of the most famous representatives of this material class, as it is the first realization of a molecular metal [3, 4]. Its properties have been studied by a number of methods and groups until recently, because of the intriguing interplay between electronic correlations, structural instabilities and low-dimensionality. Crystals of TTF-TCNQ consist of separated stacks of the two molecular constituents, which are parallel to the crystal *b*-axis [5, 6]. This results in almost ideally one-dimensional electronic bands [7, 8]. The charge transfer from TTF to TCNQ amounts to about 0.5-0.6 electrons resulting in a metallic ground state at room temperature [9]. Upon cooling the material undergoes a charge density wave transition and finally develops into an insulating ordered state below 38K [6, 9].

Metallic systems, in general, are characterized by an electron gas, i.e. the conduction electrons which can move freely and carry electrical current. Collective excitations (density fluctuations) of such an electron gas can occur at characteristic energy, ω_p, and are called plasmons. These plasmon show an inherent momentum dependence, often called plasmon dispersion. For ordinary metals, the generic behavior of the plasmons in the long wavelength limit is expected to be [10, 11]:

$$\omega_p(\mathbf{q}) = \omega_p(0) + \frac{3}{5} \frac{v_f^2}{m\omega_p(0)} q^2. \tag{1}$$

Thereby, v_F and m denote the (averaged) Fermi velocity and the electron mass, respectively. Thus, the plasmon dispersion and its anisotropy harbors information on the Fermi surface. We note that a positive quadratic plasmon dispersion has been observed in many systems, among them also correlated electron systems, and it has been used to achieve Fermi surface shape and anisotropy in some systems [12–15]. On the other hand, deviations from this plasmon dispersion reflect renormalization of the conduction electrons, and offer a way to study the effects of e.g. local field effects, electronic correlations, or charge density fluctuations etc [16–19].

The plasmon dispersion in the one-dimensional molecular metal TTF-TCNQ has been determined at room temperature some time ago [20], and it has been reported that the plasmon dispersion is negative, contrary to the expectation above. This has been ascribed to the impact of the one-dimensional nature of the material in conjunction with the rather localized electronic states typical of a molecular material [20–22]. More recent

calculations [23, 24] indicate, that this negative dispersion is rather temperature independent, i.e. it is expected to show up below and above the charge density wave transition. This suggests that the opening of the charge density wave gap has minor impact on the collective plasmon excitation.

The traditional method to determine the plasmon dispersion experimentally is electron energy-loss spectroscopy (EELS) or inelastic electron scattering [11]. The cross section of EELS is proportional to the so-called loss function $Im(1/\epsilon(q,\omega))$, $\epsilon(q,\omega)$ is the dielectric function. There are numerous examples where momentum dependent EELS measurements have provided valuable insight into the electronic properties of the materials under investigation [12, 16, 25–28]. Here, we present the determination of the plasmon dispersion of TTF-TCNQ at 20 K below the charge density wave phase transition. We show that the plasmon energy is upshifted in comparison to the value at room temperature. In contrast, the momentum dependence of the plasmon energy hardly changes and is most likely connected to the quasi one-dimensional nature of the electronic degrees of freedom.

2. Experimental

Our EELS studies in transmission require thin, freestanding films with a thickness of about 100 nm. We have prepared such films via thermal sublimation of TTF-TCNQ powder (purchased from Sigma-Aldrich) in vacuum (10^{-7} mbar). As substrate we have used NaCl single crystals. We followed previous studies [29, 30] which demonstrated that highly ordered thin films can be achieved in this manner. The freestanding films were obtained by dissolution of the NaCl substrate in distilled water. The floated-off films were mounted onto standard electron microscopy grids, and finally transferred into our spectrometer. Electron diffraction profiles taken with our spectrometer confirmed the strong anisotropic structure of the films.

All measurements were carried out using a dedicated 172 keV spectrometer described in detail elsewhere [31, 32]. We note that at such high primary beam energy only singlet excitations are possible. The energy and momentum resolution were chosen to be 85 meV and 0.04 Å^{-1}. The pressure in the spectrometer was about $2*10^{-10}$ mbar, and all loss data have been measured at low temperature (20 K) as well as at room temperature (300 K) to determine the temperature dependence.

Since organic materials often are damaged by fast electrons, we repeatedly checked our samples for any sign of degradation. Sample degradation was followed by observation of an increasing amorphous-like background in the electron diffraction profiles and a change of spectral weight in the excitation spectra around the plasmon. It turned out that under our measurement conditions the spectra remained unchanged for about 5 hours. Samples that showed any signature of degradation were not considered further but replaced by freshly prepared thin films. Data from different films were reproducible.

3. Results and discussion

The TTF-TCNQ films grown by vacuum sublimation as described above have a bi-oriented or twinned nature [29, 30]. They consist of crystallites that are predominantly oriented with their *b*-axis along the [110] direction of the NaCl substrate [20, 29, 30]. This anisotropy has been confirmed in the electron diffraction profiles and is additionally observed via the energy position of the plasmon. In figure 1, we show representative loss data of TTF-TCNQ, taken at 20 K and a momentum transfer of 0.125 Å^{-1}. We note that this momentum value is still small enough to represent the so-called optical limit. The data labeled with 0 degree have been taken with the momentum transfer vector oriented in the b-direction of the films. This corresponds to optical measurements with a light polarization vector in the same direction. A clear plasmon peak is observed with a maximum of about 0.78 eV. Changing the angle of the momentum vector as indicated in the figure results in an energy shift of the plasmon to lower energies. This is qualitatively expected for a one-dimensional metal, and it has been observed at room temperature for TTF-TCNQ previously [20–22, 33]. The anisotropy as given in figure 1 is in very good agreement to the previous data [20], which indicates a very similar sample quality. Moreover, the energy position of the plasmon with the momentum vector along the *b*-axis corresponds very well to optical reflectivity data which have been measured on single crystals [34, 35]. The deviation of our plasmon position to that of the reflectivity edge is less that 50 meV, which demonstrates the highly ordered nature of our films, i.e. the data well represent the collective plasmon excitation along the b-direction of the material.

In figure 2 we show the momentum evolution of the plasmon in TTF-TCNQ along b-direction and at 20 K. The data clearly exhibit energy variations upon increasing momentum transfer. Starting with a slight energy increase, the plasmon finally moves to lower energies, i.e. it disperses negatively. This is further illustrated in figure 3, where we depict the plasmon energies as a function of momentum transfer. In addition, equivalent data taken at 300 K are included. These 300 K data are in very good agreement to previous measurements [20].

Figure 1. Measured loss function of TTF-TCNQ at 20 K. The momentum transfer value is 0.125 $\mathring{A}^{-1}$, which is close to the optical limit. The direction of the momentum transfer has been rotated in the film plane by in total 45 degrees with respect to the b-direction to show the anisotropy of the loss function as a result of the highly ordered film growth.

Figure 2. Momentum dependence of the plasmon in TTF-TCNQ along b-direction. The data have been taken at 20 K. The momentum transfer value is indicated, respectively.
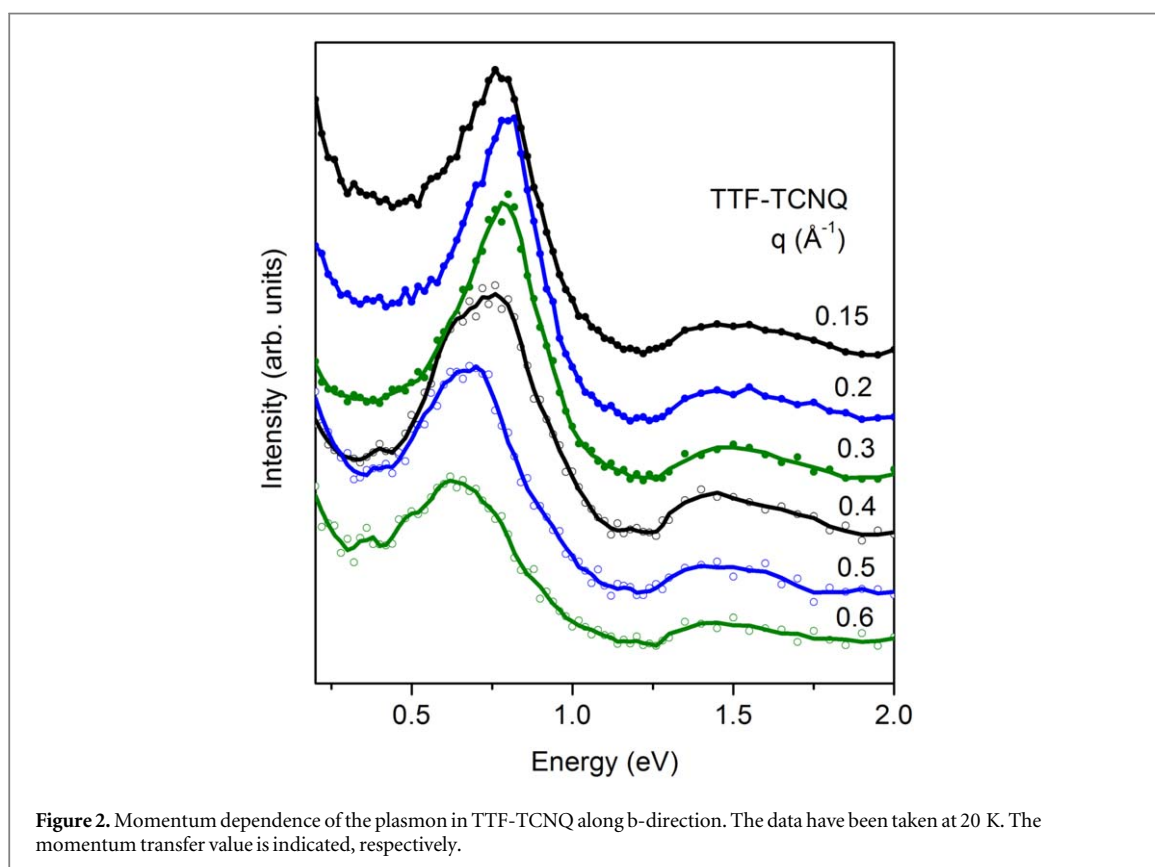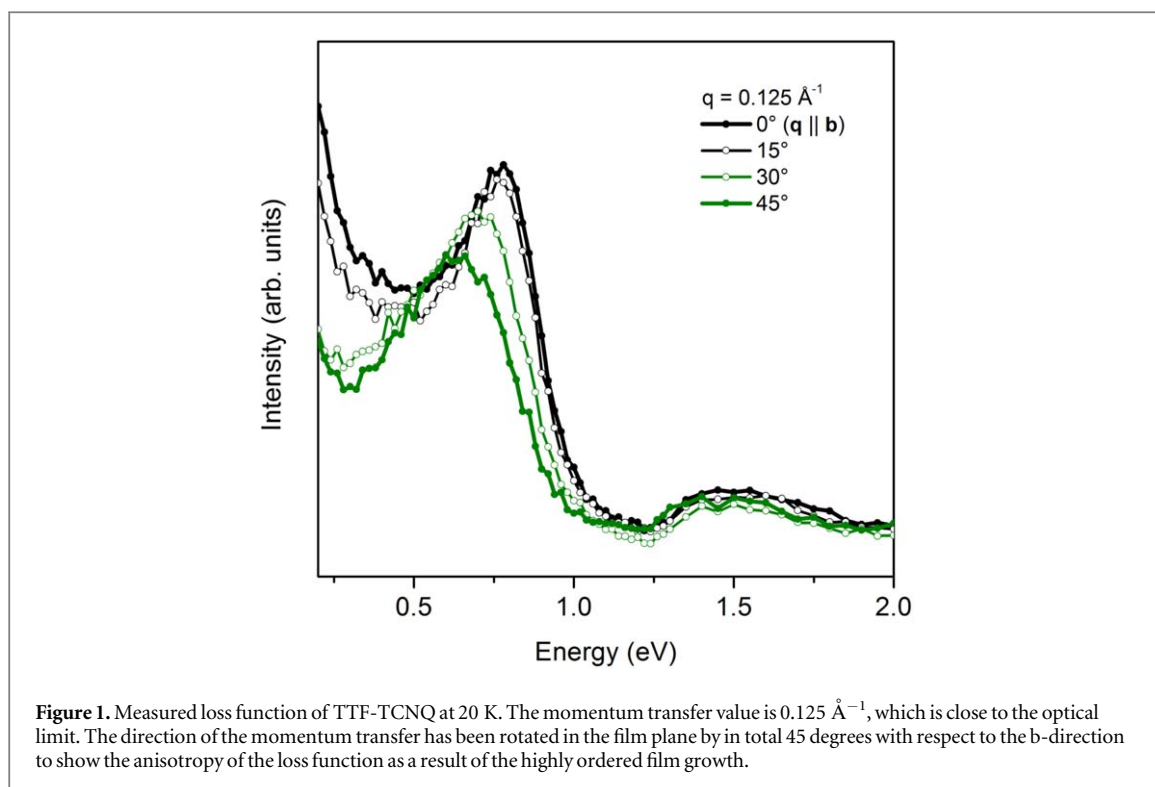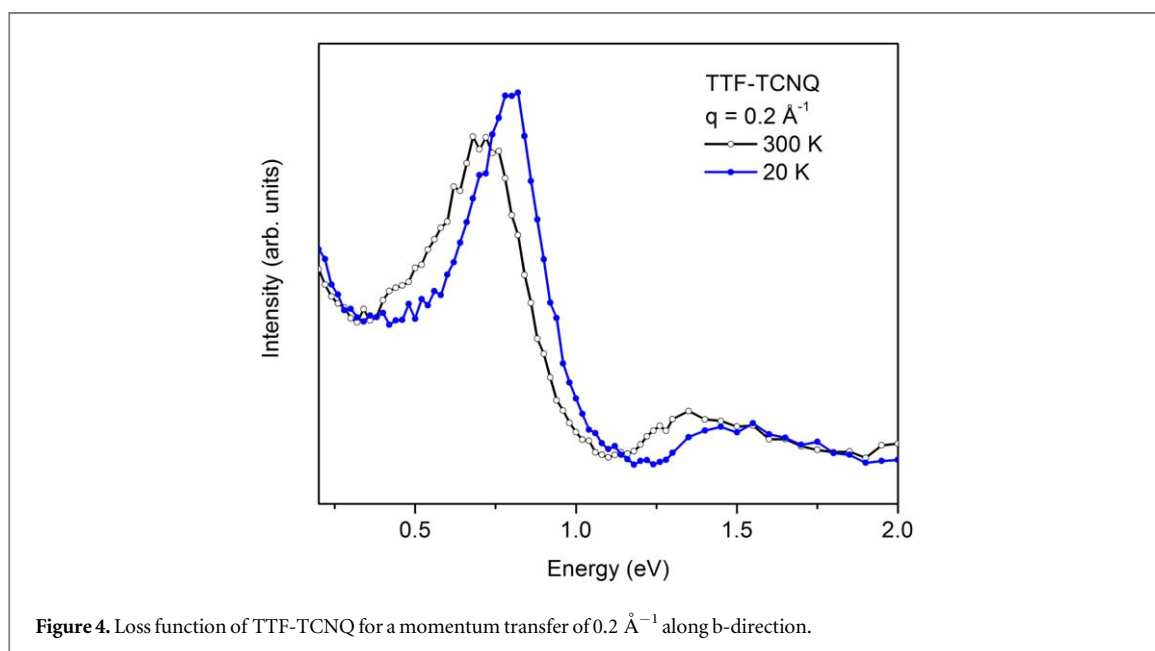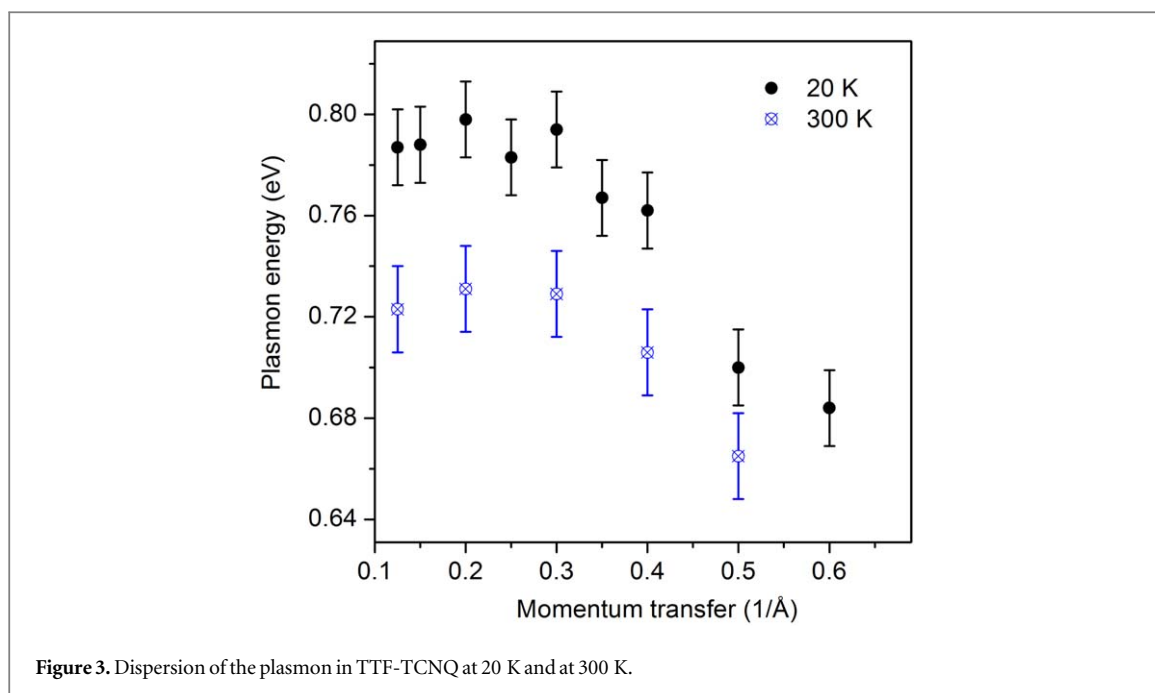
Figure 3 demonstrates a rather complex plasmon behavior in TTF-TCNQ. Independent of temperature, the plasmon dispersion is negative at higher momentum transfers, while initially—up to about 0.3 $\mathring{A}^{-1}$ - it slightly increases/ stays rather constant. Moreover, there is a plasmon energy increase upon lowering the temperature. This energy increase going to lower temperature is exemplarily presented in figure 4 for a selected momentum value. The temperature dependent energy variation is in good quantitative correspondence to what has been reported from optical reflectivity measurements [34, 35]. However, the explanation of this behavior is not settled

Figure 3. Dispersion of the plasmon in TTF-TCNQ at 20 K and at 300 K.

Figure 4. Loss function of TTF-TCNQ for a momentum transfer of 0.2 $\mathring{A}^{-1}$ along b-direction.

yet. Based upon the proportionality of the plasmon energy to the square root of the conduction electron density $\omega_p \propto \sqrt{n}$ [10, 11], it has been suggested that the energy increase of the plasmon might be due to an increase of the electron density as a consequence of lattice contraction [34]. On the other hand, the lattice expansion of TTF-TCNQ going from low to high temperatures is very small, high resolution diffraction results show that it is smaller than 4% [36, 37], and thus the energy increase as exhibited in figure 3 cannot be explained on the basis of this effect alone. Alternatively, the analysis of optical reflectivity data has indicated that the plasmon energy remains unchanged as a function of temperature, the observed shifts are rather a consequence of the temperature dependent changes of the background dielectric polarizability in the material [35], which screens the plasmon oscillation. This background dielectric polarizability can change when the spectral weight of inter-band transition or their energy change as a function of temperature, e.g. induced by the lattice expansion. Again, since the lattice expansion of TTF-TCNQ is rather small, it is unlikely that it causes big enough changes of the background dielectric polarizability to account for the plasmon energy change.

A temperature dependent increase of the plasmon energy has also been observed for another system, which is characterized by a charge density wave ground state: 2H-TaSe$_2$ [38, 39]. In this case, this energy shift has been associated with the opening of the charge density wave gap in the electronic spectrum [38]. Within a simple
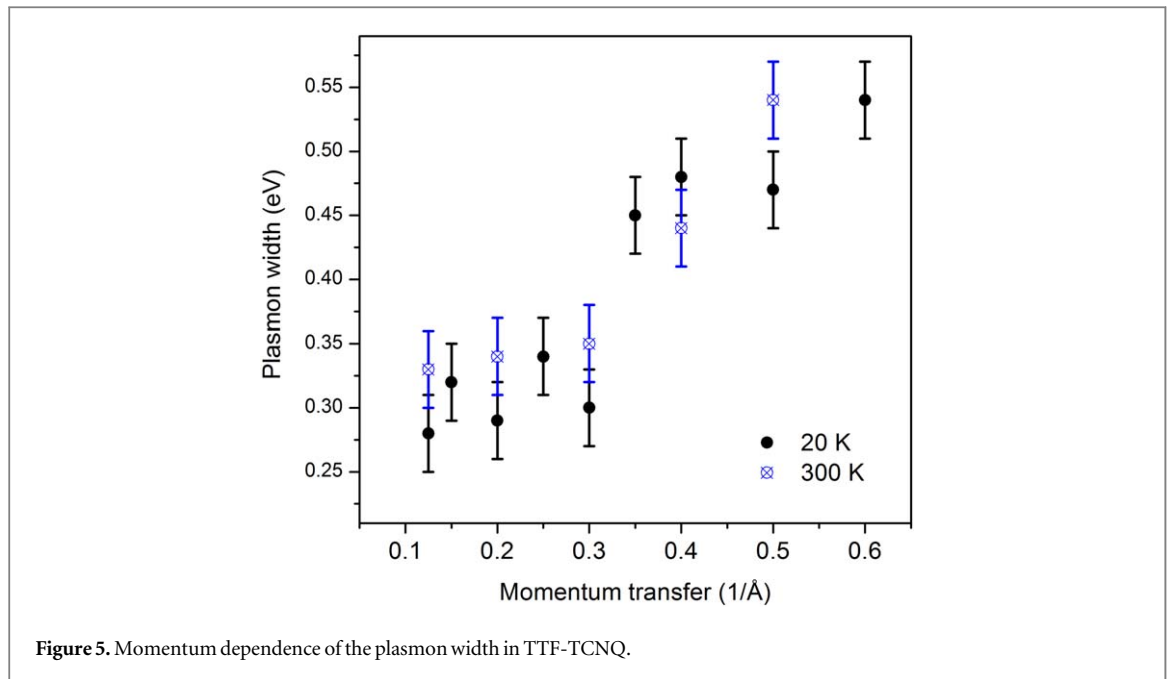
Figure 5. Momentum dependence of the plasmon width in TTF-TCNQ.

consideration, the plasmon energy, ω_p, as seen in the loss function would shift to $\tilde{\omega} = \sqrt{\omega_p^2 + E_g^2}$ (E_g denotes the energy gap). The charge density wave gap for TTF-TCNQ has been measured to be about 0.14eV [40]. Taking into account a plasmon energy at 300 K of 0.72 eV (our data) or 0.75 eV (Ritsko *et al* [20]), this simple estimate yields an energy upshift to about 0.74eV or 0.76 eV, i.e. the opening of the charge density wave gap also is not able to quantitatively explain the experimental findings. Interestingly, recent finite temperature calculations of the collective modes in TTF-TCNQ [24] report an energy increase around 0.2 Å^{-1} of about 10% going to lower temperatures, in quite good agreement to our data. There, this energy shift has been assigned to the higher rate of excitation of electron-hole pairs for higher temperatures [24].

At room temperature, i.e. far above the charge density wave gap, the plasmon energy can be taken to derive the (optical) conductivity in the low frequency limit and the effective mass of the charge carriers. The conductivity, $\sigma(0)$, of a simple metal is related to the plasmon via [35]:

$$\sigma = \epsilon_0 \epsilon_\infty \omega_p^2 \Gamma^{-1}. \tag{2}$$

Here, ϵ_∞ is the background dielectric constant and Γ is the spectral width of the plasmon (see also below). Taking into account $\omega_p = 0.72$ eV, $\Gamma = 0.33$ eV (see figure 5 and below) and $\epsilon_\infty = 2.5$ [35], we arrive at a (dc) conductivity of about 470S/cm. This is in very good agreement to conductivity measurements along the crystal b-direction [41]. Also, an estimate of the charge carrier effective mass, m^* can be obtained , since [35]:

$$\omega_p^2 = ne^2 / \epsilon_0 \epsilon_\infty m^*. \tag{3}$$

To do so, we assumed a charge transfer from TTF to TCNQ molecules of about 0.6 [9], resulting in a charge carrier density of about $2.38 \cdot 10^{21}$ cm^{-3}. This yields a relatively large effective mass of about 2.2 times the bare electron mass. An effective mass of this size is not surprising for a molecular material with relative small band width, as e.g. provided by band structure calculations or angular resolved photoemission data [7, 8]. This value also is in good correspondence to estimates from optical data [35].

We now come back to the momentum dependence of the plasmon in TTF-TCNQ. For other quasi-one-dimensional systems, the plasmon dispersion has also been measured [13, 42, 43]. In all of these cases, the plasmon dispersion is clearly positive in contrast to the case of TTF-TCNQ presented here.

On the other hand, it was realized that there are limitations to equation (1) for low conduction electron densities due to the neglect of exchange and correlation effects. There have been quite a number of proposals how to meet the low electron density limit by introducing so-called local field corrections [44–48]. However, the inverse scattering rate of the charge carriers in TTF-TCNQ has been reported to change linearly with temperature [35], which signals a minor importance of correlation effects for the electronic properties. Thus, as the plasmon dispersion is negative at room temperature too, we exclude correlation effects to be responsible for this behavior.

Another effect that can impact the plasmon dispersion is the influence of inter-band excitations and their momentum dependence. In some cases they have been shown to change the plasmon dispersion significantly [19, 49, 50]. For TTF-TCNQ, however, the excitations above the plasmon energy hardly change upon

momentum transfer (see figure 2). This renders it unlikely that the negative dispersion is due to their momentum dependent impact.

Model calculations of the plasmon dispersion in quasi-one-dimensional systems in the random-phase approximation have been reported by Williams and Bloch [33]. In their publication, they considered the impact of crystal local-field effects and that of the conduction electron localization, i.e. whether it is free-electron-gas-like or whether it can be described using a tight-binding approach. For free electrons, still predict a quadratic plasmon dispersion, as expected for simple metals. Going to a tight-binding band structure however, as it is appropriate for TTF-TCNQ, the plasmon dispersion is strongly renormalized and even can become negative. These model calculations thus already provide a rather good qualitative understanding of the corresponding data. More recent calculations of collective modes in TTF-TCNQ within a tight-binding formalism confirm these trends, most importantly they also predict a negative plasmon dispersion [23, 24]. Moreover, in agreement with our data, the slope of the negative dispersion is hardly dependent on temperature. The fact that the charge density wave gap does not lead to clear changes can be understood by the fact that the gap is rather small and that is does almost not change the number of electrons which contribute to the collective plasmon excitation.

Finally, we consider the spectral width of the plasmon excitations in TTF-TCNQ. From figure 2 above it becomes clear that there is an increase of the spectral width at higher momentum transfer values. In order to quantify this, we have modeled the plasmons in the loss function, $Im(1/\epsilon)$, using a simple Drude formula [31, 51]: $\epsilon(\omega) = 1 - \omega_p^2/(\omega^2 + i\gamma\omega)$. The spectral width, γ, as obtained from these fits is depicted in figure 5. This figure demonstrates that initially, up to about 0.3 $\mathring{A}^{-1}$, the energy width of the plasmon does hardly change, while for higher momentum values it increases clearly. Furthermore, there is only little temperature dependence of this behavior. At this point we emphasize that the behavior as shown in figure 5 disagrees with the previous data [20], where a linear increase of the plasmon width has been reported. The reason for this discrepancy is unclear, we can only speculate that it might be related to the different momentum resolution in the measurements. The previous momentum resolution [20] was about 50% worse than in this contribution.

In a quasi-one-dimensional system, such as TTF-TCNQ, the collective plasmon excitation does not enter the continuum of excitations of electron-hole pairs [23, 24, 33] as would be expected for a three-dimensional case. Thus, there is no Landau damping of the plasmons. Therefore, other mechanisms must be responsible for the observed behavior, in particular for the strong increase of plasmon damping at larger momentum values. In general, there are several possible contributions to the plasmon damping, e.g. the plasmon decay into inter-band transitions, scattering by impurities or defects, or scattering by phonons. In consideration of the momentum dependence, the most likely mechanism is a plasmon decay due to inter-band transitions. This requires an energy band in TTF-TCNQ which is located below the Fermi energy by about the value of the plasmon energy (i.e. about 0.75 eV, cf [35]). While this is not expected from band structure calculations, experimental data obtained by angular resolved photoemission spectroscopy have provided evidence for a band at about 0.75 eV below the Fermi energy [8].

4. Summary

We have studied the plasmon dispersion as well as the momentum dependence of plasmon width/damping in the quasi one-dimensional metal TTF-TCNQ. The slope of the plasmon energy at room temperature agrees well with optical data. The plasmon dispersion is rather temperature independent and is in good agreement to model calculations presented previously. An energy upshift upon going to lower temperatures is observed, a quantitative, microscopic explanation however is not available yet. Upon increasing momentum, the plasmon spectral width initially remains constant before it increases visibly above a momentum transfer of about 0.3 $\mathring{A}^{-1}$. This suggests an additional damping mechanism which sets in at this momentum, which most likely is due to inter-band transitions..

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